Supporting information

Chemical Recycling of Unsaturated Polyester Resin and Its Composites via Selective Cleavage of ester Bond

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Materials:

Poly-maleic anhydride-phthalic anhydride-1,2-propylene glycol cross-linked with styrene (PMPPS) and its glass fiber reinforced polymer composites (GFRP) were provided by ZXTR Science & Technology CO., LTD. (Changzhou, Jiangsu Provence, China). Acetic acid and aluminium chloride were purchased from Aladdin (Shanghai, China). Methanol, ethanol, n-propanol, i-propanol, acetone, ethyl acetate, and tetrahydrofuran were purchased from Alfa Aesar (China) and used without further purification. Ferric chloride, zinc chloride, magnesium chloride and copper chloride were purchased from J&K scientific LTD. (Beijing, China). Aluminium sulphate, aluminium nitrate and aluminium acetate was supplied by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

Characterization:

Fourier transform infrared (FT-IR) analysis of the samples was performed using BRUKER TENSOR 27 spectrophotometer in the range from 400 to 4000 cm^{-1}. Solid-state NMR spectra of all samples were recorded on a Bruker Avance Ⅲ spectrometer operating at 600 MHz; ^{13}C-NMR spectra of product 2 was monitored on a Bruker Avance Ⅲ spectrometer operating at 400 MHz. Elemental analysis was carried out using Vario EL CUBE elemental analyser made in German. A thermo iCAP6300 inductively coupled plasma emission spectrometer (ICP) was used to determine the content of various elements in the samples. The number average molecular weights (Mn), weight average molecular weight (Mw) and polydispersities (PDI) were measured by GPC using THF as the eluent at 35 °C. Calibration was against polystyrene standards. A JSM-7001F scanning electron microscope (SEM) was used to observe the morphology of virgin glass fibers and recycled glass fibers.

Synthetic procedure of PMPPS

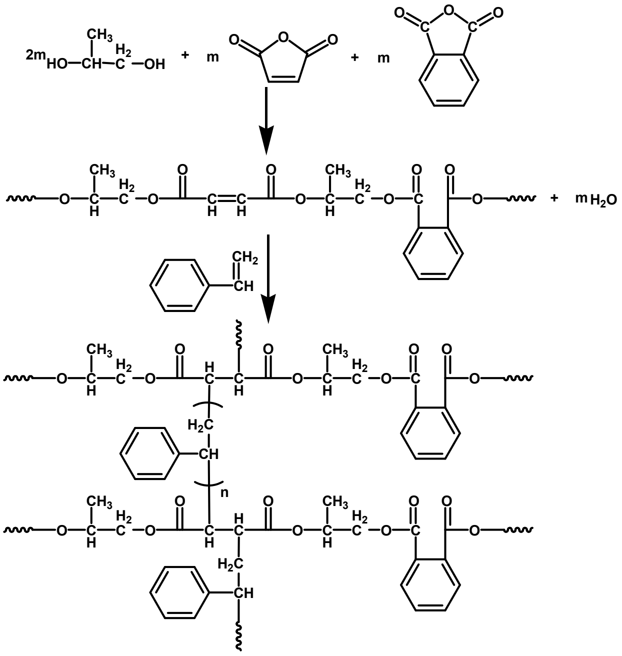
PMPPS was synthesized by two steps: linear polycondensation products were produced by unsaturated anhydrides (maleic anhydride), saturated anhydrides (phthalic anhydride) and diols (1,2-propylene glycol); then, the unsaturated bond in the backbone provides sites for reaction with vinyl monomers (styrene) using free-radical initiators, thereby, leading to the formation of a three-dimensional network (SI Scheme 1).

Proof of acyl exchange reaction between ester bond and acetic acid

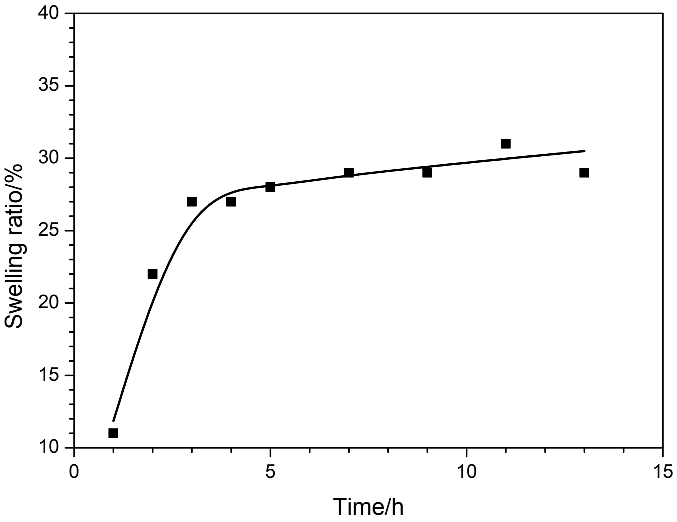
As shown in SI Figure 9, the acyl exchange reaction between ester bond and acetic acid was proved by gas chromatography. Ethyl butyrate was selected as model compound. The acyl exchange reaction between ethyl butyrate and acetic acid was carried out under the condition of $AlCl_3$ as catalyst, 180 ^oC and 2 h. The ethyl acetate and ethyl butyrate were detected in SI Figure 9 (a) and (b), respectively. The retention time of ethyl acetate and ethyl butyrate were 10.13 min and 13.86 min, respectively. The mixture solution of ethyl butyrate and acetic acid was characterized in SI Figure 9 (c). The retention time of acetic acid was 10.45 min. As shown in SI Figure 9 (d), the content of ethyl butyrate decreased obviously, meanwhile ethyl acetate appeared after reaction. The conclusion indicated the acyl exchange reaction between ester bond and acetic acid can reacted under the degradation system and conditions.

Experimental section:

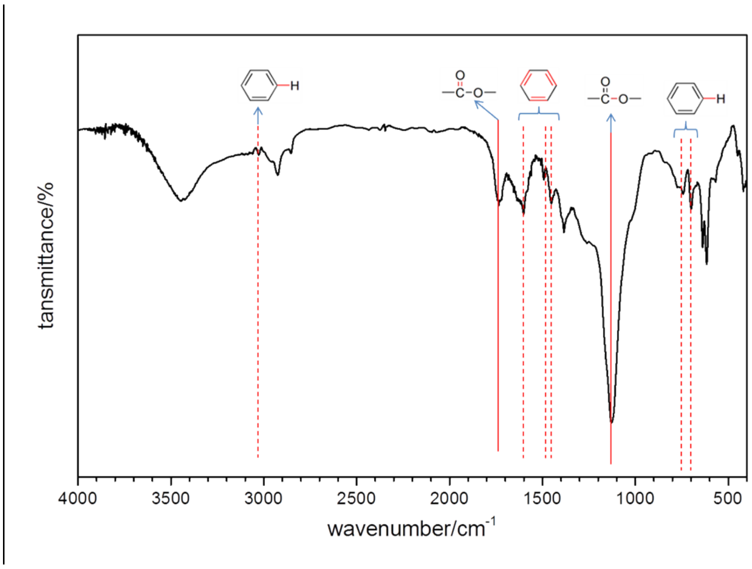
The decomposition of PMPPS and GFRP were tested in a Teflon-lined autoclave with a content of 10ml. In each test run, PMPPS chips (0.8 g, 10 mm × 10mm × 6 mm of cuboid form) or GFRP (1.5 g), $AlCl_3$ (0.5 g) and acetic acid (4.5 g) were added, and the degradation was carried out at 180 ^oC for 12 hours. In the cases of PMPPS degradation, after the decomposition, the reaction mixture dissolved in tetrahydrofuran (THF) by ultrasonic, and aluminum catalyst (product 1), which is insoluble in THF, was collected by filtering. Water was then added into THF solution acting as precipitant, and the flocculent-like organic product (product 2) was precipitated from the solution. Product 2 was collected by removing THF with rotary evaporation at 40 ^oC. Product 3 that is soluble in water was collected after removing water by rotary evaporation at 60 ^oC. The compositions of product 1, 2 and 3 were identified by IR, NMR and ICP. In the cases of GFRP degradation, besides the degradation products, the glass fibres were collected and washed by 3 times with 10 ml THF, followed by washing with 10 ml 10 wt% diluted hydrochloric acid for 3 times.



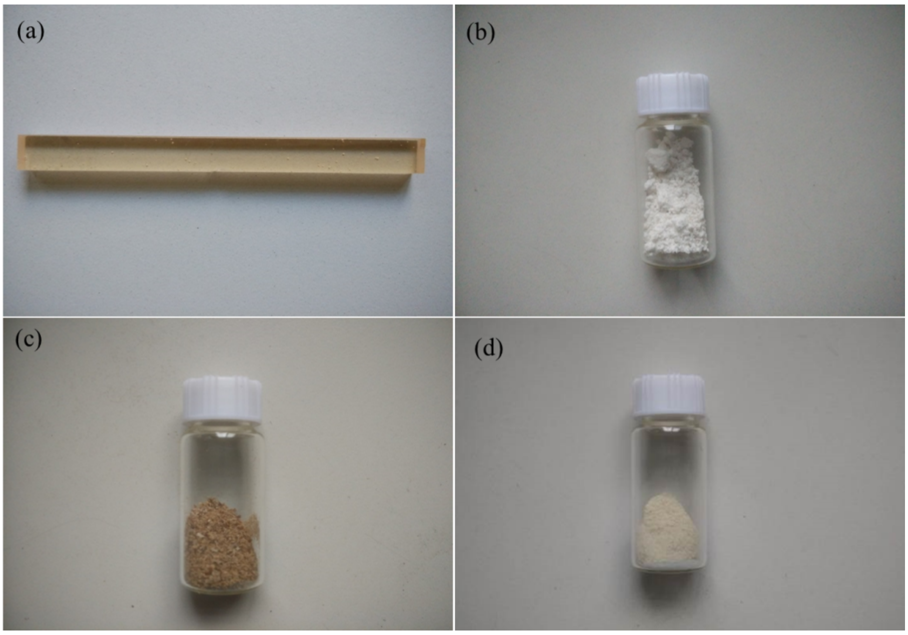
SI Scheme 1. Synthesis process of PMPPS.



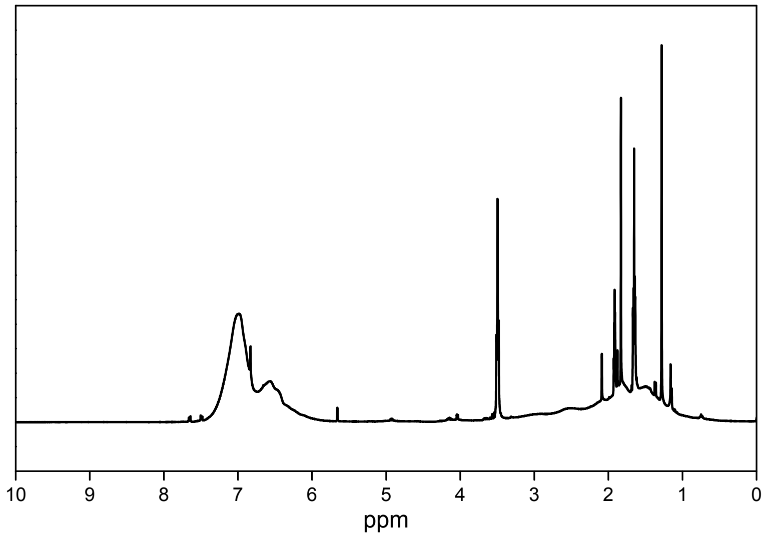
SI Figure 1. Swelling of PMPPS in acetic acid. Reaction Temperature: 180 °C.



SI Figure 2. FT-IR spectroscopy of swollen PMPPS.

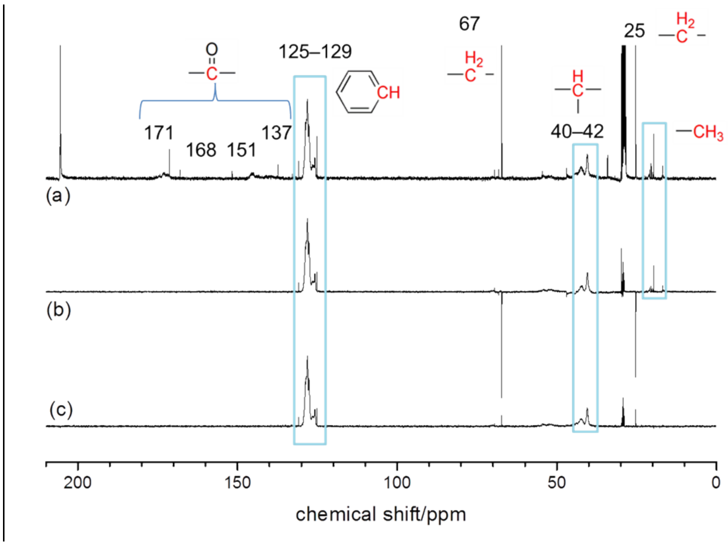


SI Figure 3. Pictures of PMPPS and its degradation products: (a) PMPPS (b) product 1 (c) product 2 (d) product 3.



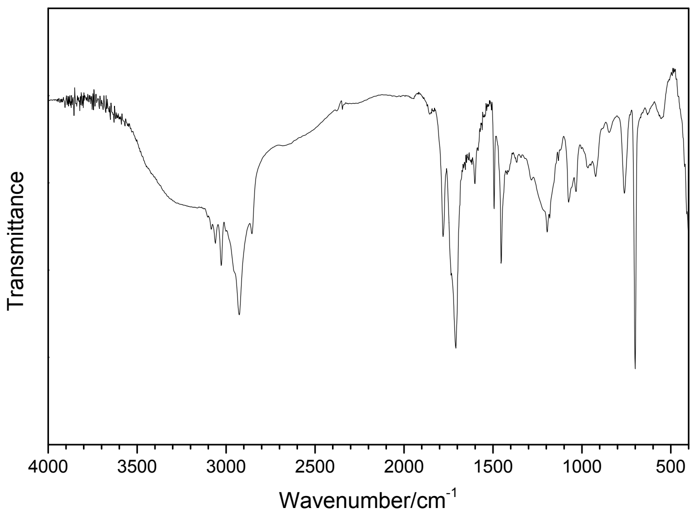
SI Figure 4. ^{1}H-NMR of product 2.

The ^{1}H NMR spectra of product 2 are shown in **SI Figure 4**. The benzene ring is present in the product 2 significantly.

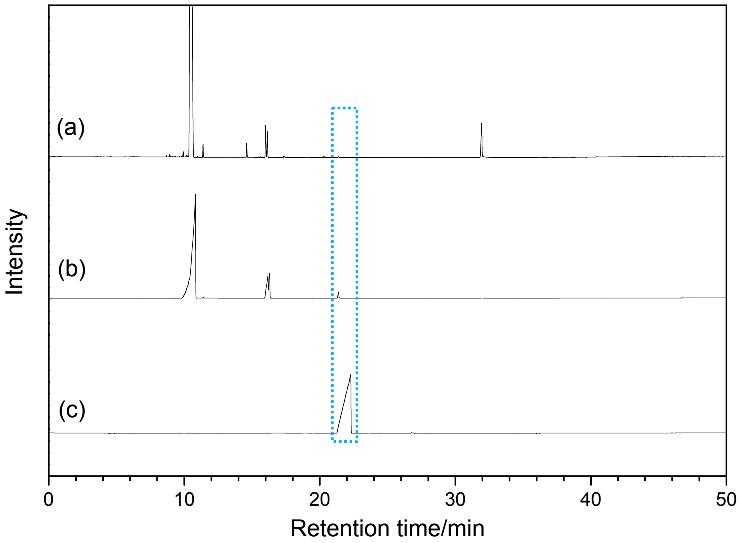


SI Figure 5. ^{13}C-NMR of product 2: (a) primary spectrum, (b) DEPT 135, (c) DEPT 90.

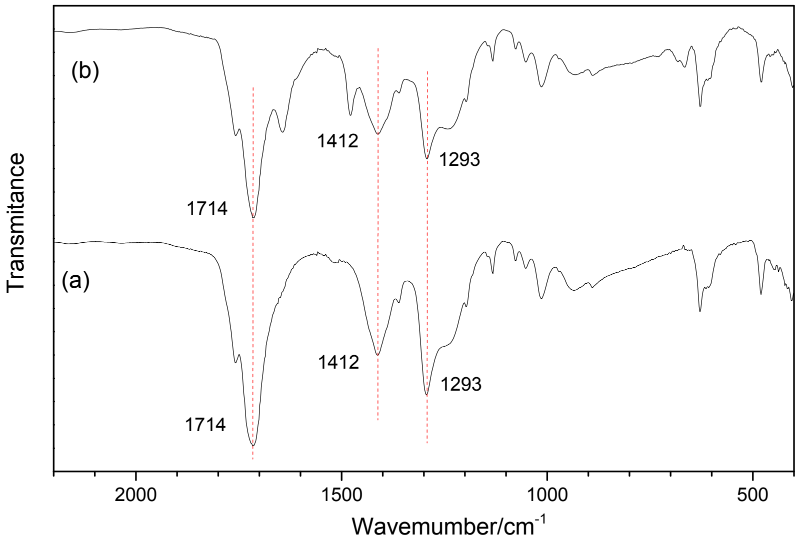
The carbon skeleton of product 2 has been studied using ^{13}C-NMR including primary spectra, DEPT 135 and DEPT 90. As shown in **SI Figure 5**, peaks at 171, 168, 151 and 137 ppm are assigned to C=O since the quaternary carbon does not appear in DEPT spectrum. The most prominent signal of carbons deprived from PMPPS is from aromatic rings between 125 and 129 ppm. The set of peaks should be attributed to –CH of benzene ring because they appear in DEPT 90. Chemical shift of 67 ppm is characteristic peak of 1,2-propylene glycol and its derivatives. The peak appears in the DEPT 135, and the negative peak of 67 ppm should be –CH_2 of 1,2-propylene glycol. The chemical shift around 42 ppm and 40 ppm can be assigned to maleic acid derivatives which derived from the double bond addition reaction of maleic acid and styrene. These peaks should be assigned to –CH. The main components of product 2 should be polyaddition product of maleic anhydride and styrene.



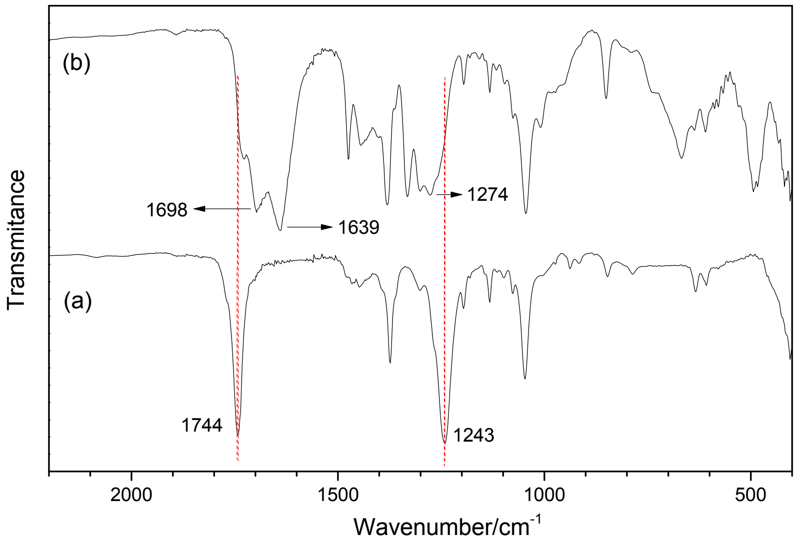
SI Figure 6. FT-IR of the further degradation products of product 2. Reaction condition: 10 wt% $AlCl_3/CH_3COOH$, 180 °C, 12 h.



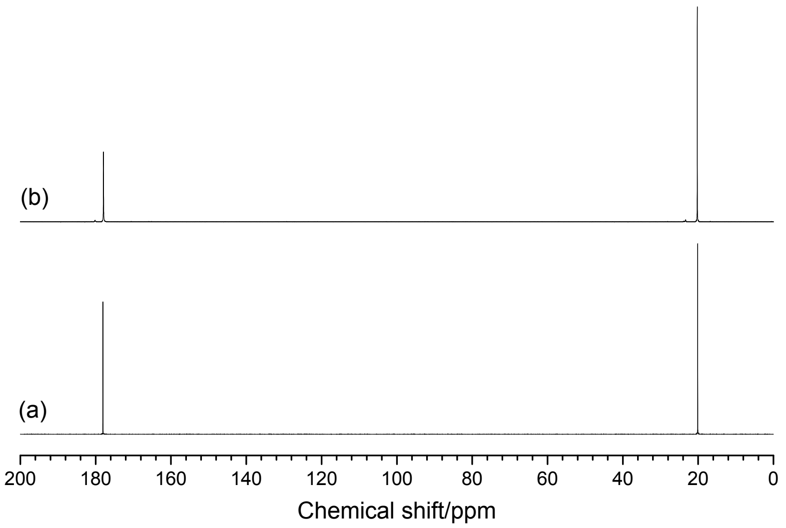
SI Figure 7. GC graphs of: (a) degradation products of PMPPS (reaction condition: 10 wt% $AlCl_3/CH_3COOH$ (5g), PMPPS chips (0.8 g), 180 ^oC, 12 hours); (b) the transformation of 1,2-propylene glycol diacetate in the 10 wt% $AlCl_3/CH_3COOH$ system after reaction for 2 hours at 180 ^oC; (c) 1,2-propylene glycol diacetate.



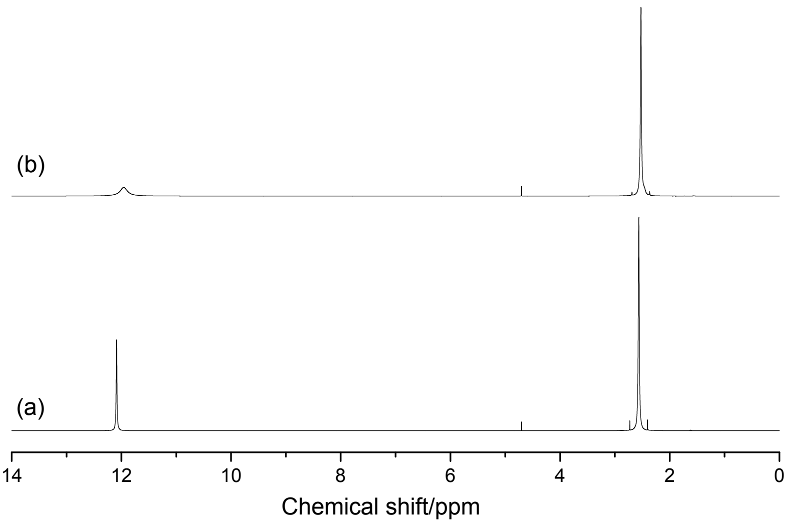
SI Figure 8. FT-IR of (a) acetic acid, (b) saturated $AlCl_3/CH_3COOH$ solution.



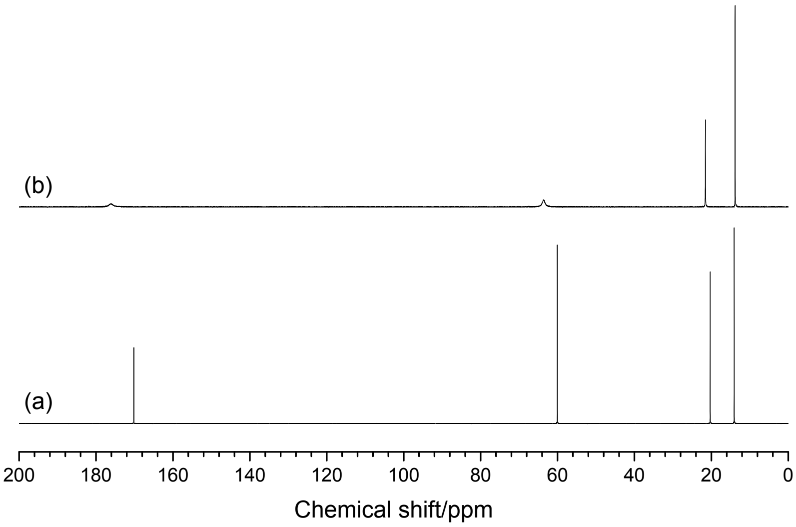
SI Figure 9. FT-IR of (a) ethyl acetate, (b) saturated $AlCl_3$/ ethyl acetate solution.



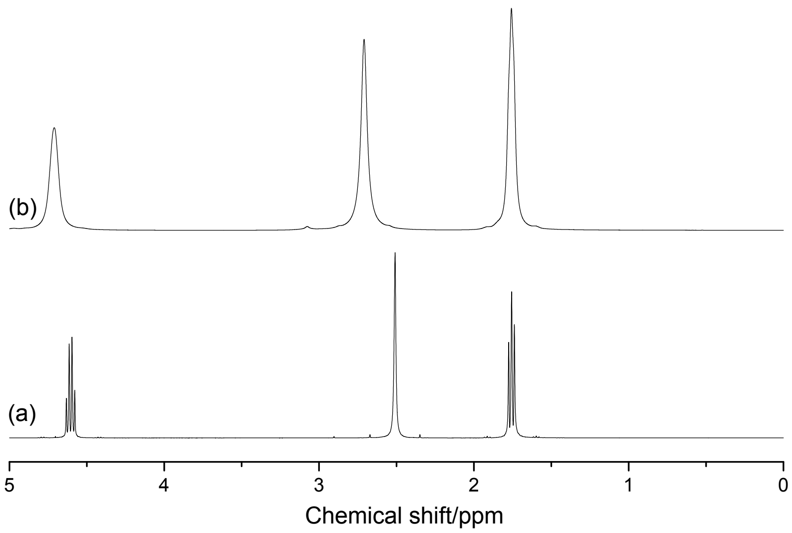
SI Figure 10. ^{13}C-NMR of (a) acetic acid, (b) saturated $AlCl_3/CH_3COOH$ solution.



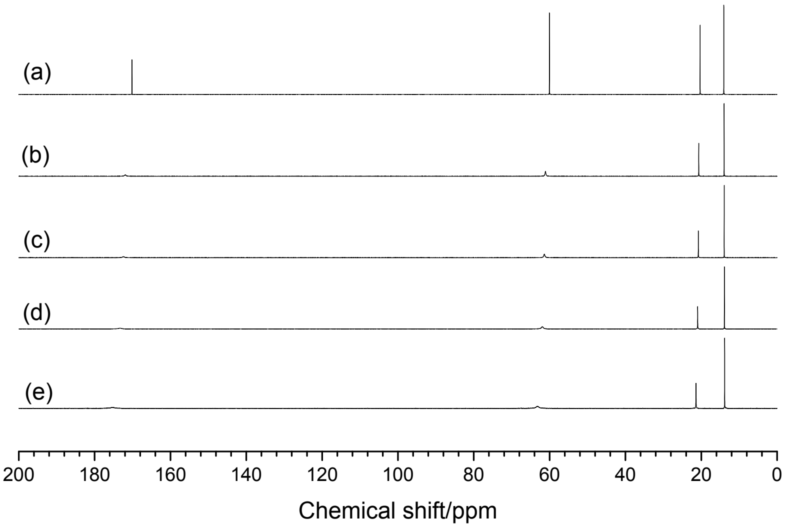
SI Figure 11. ^{1}H-NMR of (a) acetic acid, (b) saturated $AlCl_3/CH_3COOH$ solution.



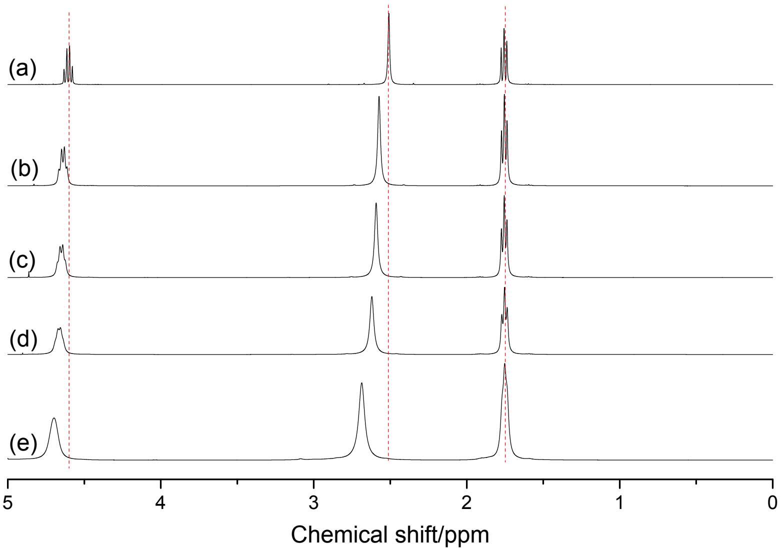
SI Figure 12. ^{13}C-NMR of (a) ethyl acetate, (b) saturated $AlCl_3$/ ethyl acetate solution.



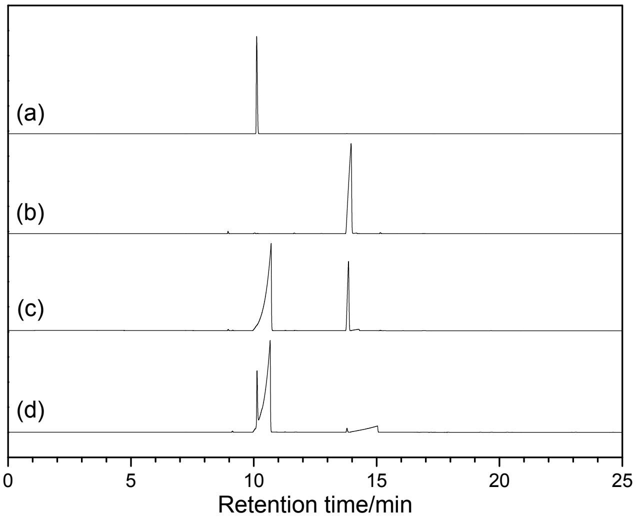
SI Figure 13. ^{1}H-NMR of (a) ethyl acetate, (b) saturated $AlCl_3$/ ethyl acetate solution.



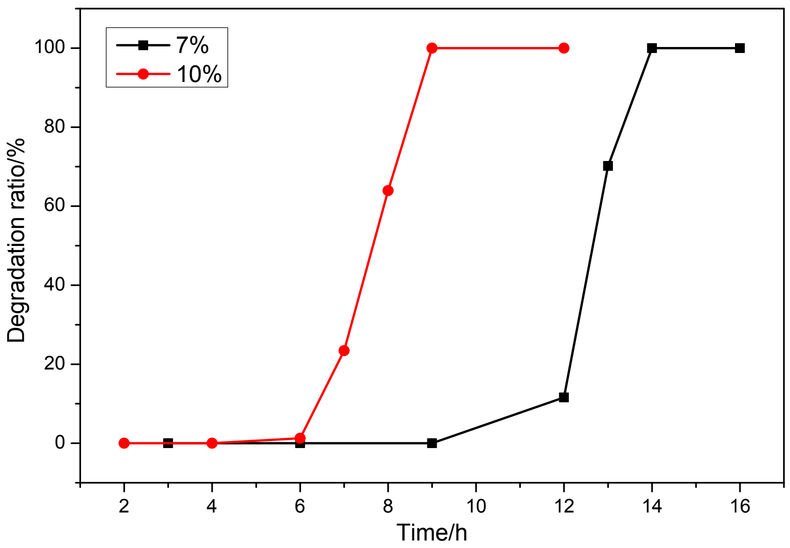
SI Figure 14. ^{13}C-NMR of $AlCl_3$/ ethyl acetate solution of different mole ratio: (a) ethyl acetate, (b) 1:10, (c) 1:8, (d) 1:6, (e) 1:4.



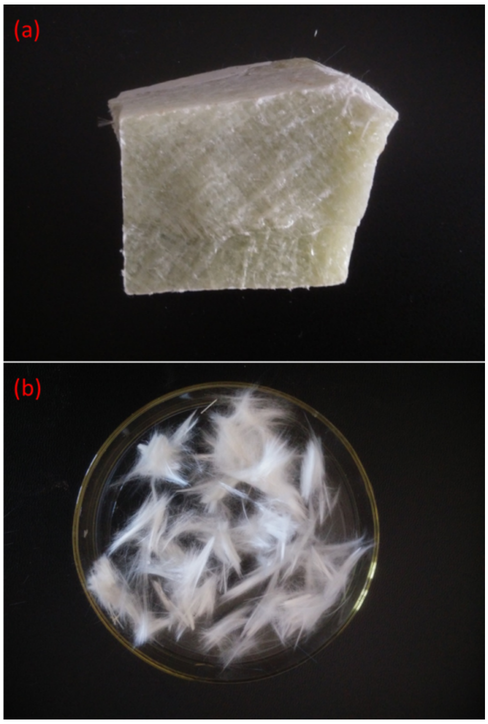
SI Figure 15. ^{1}H-NMR of $AlCl_3$/ ethyl acetate solution of different mole ratio ($AlCl_3$: $CH_3COOCH_2CH_3$): (a) ethyl acetate, (b) 1:10, (c) 1:8, (d) 1:6, (e) 1:4.



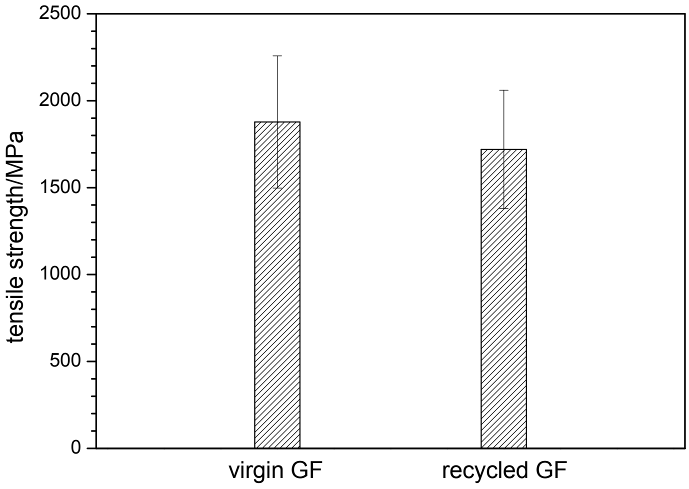
SI Figure 16. Acyl exchange reaction between ester bond of ethyl butyrate and acetic acid catalyzed by $AlCl_3$. GC graphs of (a) ethyl acetate, (b) ethyl butyrate, (c) mixture of acetic acid and ethyl butyrate (before reaction) , (d) reaction products of acetic acid and ethyl butyrate. The reaction conditions: $AlCl_3$: 0.5 g; Acetic acid: 4.5 g; ethyl butyrate: 1 g; reaction temperature: 180 ^{o}C; time: 2 h.



SI Figure 17. PMPPS degradation in 7% and 10% $AlCl_3/CH_3COOH$ system at 180 °C.



SI Figure 18. Recycled glass fibres from GFRP. Degradation condition: 10 wt% $AlCl_3$/CH_3COOH, 180 ^{o}C, 9 h. (a) GFRP, (b) recycled glass fiber.



SI Figure 19. Monofilament tensile strength of virgin GF and recycled GF. Degradation condition: 10 wt% $AlCl_3/CH_3COOH$, 180 ^oC, 9 h.

SI Table 1. The degradation of resins in metal chloride aqueous solutions.

Entry	Resin	Catalyst	wt./%	Temp./^oC	Time/h	Degradation or not
1	PMPPS	$ZnCl_2$	60	160	24	No
2	PMPPS	$ZnCl_2$	50	160	24	No
3	PMPPS	$ZnCl_2$	40	160	24	No
4	PMPPS	$ZnCl_2$	30	160	24	No
5	PMPPS	$ZnCl_2$	20	160	24	No
6	PET	$ZnCl_2$	20	160	3	No
7	PET	$ZnCl_2$	30	160	3	No
8	PET	$ZnCl_2$	40	160	3	No
9	PET	$ZnCl_2$	60	160	24	Yes
10	PET	$AlCl_3$	10	180	6	No
11	PET	$AlCl_3$	20	180	6	No
12	PET	$AlCl_3$	30	180	6	Yes

SI Table 2. the quality of the components before and after reaction. [a]

Entry	$AlCl_3$	resin	product 1	product 2	product 3
Mass/g	1.50	2.23	1.35	1.11	0.94

[a] acetic acid as solvent: 13.5 g.

SI Table 3. GPC results of product 2. [a]

Entry	M_n	M_w	M_p	M_w/M_n
Molecular weight	12891	23141	22680	1.79

[a] molecular weight and polydispersity of product 2.

SI Table 4. Acyl exchange reaction between ester bond of ethyl butyrate and acetic acid catalyzed by $AlCl_3$.

Entry	Ester	Conversation ratio/%	Yield%
1	Ethyl butyrate	97.02	-
2	Ethyl acetate	-	93.32

[a] The reaction conditions: $AlCl_3$: 0.5 g; Acetic acid: 4.5 g; ethyl butyrate: 1 g; reaction temperature: 180 ^{o}C; time: 2 h.

SI Table 5. Aluminum content of residual PMPPS in different degradation time in 7 wt% $AlCl_3/CH_3COOH$ system.[a]

Entry	Time/h	Aluminum content/wt%
1	3	0.0559
2	6	0.1154
3	9	0.1665
4	12	0.3095
5	13	0.4055

[a] Reaction temperature: 180 ^oC.

SI Table 6. Aluminum content of residual PMPPS in different degradation time in 10 wt% $AlCl_3/CH_3COOH$ system[a]

Entry	**Time/h**	**Aluminum content/wt%**
1	4	0.2218
2	5	0.2576
3	6	0.3416
4	7	0.4703

[a] Reaction temperature: 180 ^{o}C.